



Catalytic activity of NiO cathode in molten carbonate fuel cells



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ABSTRACT

Molten carbonate fuel cells (MCFCs) have attracted significant attention because of their potential contribution to the development of a sustainable and clean-energy society. MCFC performance is governed by cathodic transformation of carbon dioxide to carbonate anion in complex: gas – molten carbonate – solid surface system. Based on our recently proposed reaction mechanism together with the density functional theory (DFT) calculated activation barriers we created a simplified microkinetic model to predict the catalytic activity of the NiO cathode. Under the MCFC operation condition the cathode surface in close proximity to the triple phase boundary (TPB) is highly active towards electro-reduction of oxygen and simultaneous formation of carbonate anion. Our results explain why, despite a great effort devoted to modify the chemical composition of the cathode, a substantial increase in the MCFC performance has not been observed, and the *in-situ* oxidized nickel remains state-of-the-art cathode material.

1. Introduction

Molten carbonate fuel cells (MCFCs) are gaining increased attention from the power market as sources of highly stable electricity and as chemical energy converters able to reach high fuel-to-energy conversion efficiency, while providing beneficial near- or net-zero emission of greenhouse gasses [1,2]. In the light of this fact, MCFC is currently considered as one of the most promising fuel cell technologies for unconventional, distributed generation of clean energy in the near future. Although the MCFC technology has been successfully commercialized in industry, it is still gaining momentum to overcome its scientific immaturity, particularly related to improvement of performance and lifetime [3].

MCFC performance is to a great extent determined by the cathode which promotes complex chemistry of the reaction between carbon dioxide (CO₂) and oxygen (O₂) towards formation of a carbonate ion (CO₃²⁻), and which unfortunately is susceptible to degradation in the molten carbonate electrolyte. Numerous experiments have been reported to date, where efforts to enhance protection of NiO porous cathodes against dissolution in molten alkali carbonates were realized by modification of cathode material [4,5] or coatings [6–8]. These modifications, however, improved the chemical stability of NiO cathodes, but in turn, they lowered its electrical conductivity and decreased the overall fuel cell performance. Therefore, nickel *in situ* oxidized to NiO has not been provided an alternative and still remains state-of-the-art MCFC cathode material. Moreover, the catalytic activity of NiO

porous cathode in MCFC has not been enhanced itself, despite multiple attempts, e.g. [9]; broader review in [10], since it is broadly considered as providing the determinant contribution to fuel cell performance [10,11]. The elevated operating temperature of MCFCs (650 °C) is high enough to guarantee high activity of cathode and efficiently promote the electrochemical reaction. High loss in potential occurring at high current density probably results from limitations in mass-transfer through the porous electrode, as well as insufficient ion transfer in the molten electrolyte, rather than low catalytic activity of the cathode. The reaction mechanism of NiO cathode in the MCFC, which was a point of major concern in this case, has been revealed in our previous work [12]. On the basis of density functional theory (DFT) calculations we have shown that the transformation of CO₂ and O₂ into CO₃²⁻ in MCFC *operando* occurring through sequential Mars-van Krevelen (MvK) and Eley-Rideal (ER) mechanism at the perimeter of triple phase boundary (TPB) – a region, where electronically conducting catalyst, ionically conducting electrolyte and pore space with reactant gases are combined (see Fig. 1 for detailed explanation). Using the proposed reaction pathway and DFT calculated potential energy diagrams we identified rate-determining steps and performed Sabatier analysis to elucidate the kinetics at the NiO porous electrode in MCFC for oxygen reduction and formation of carbonate ion.

2. Results and discussion

To estimate the catalytic activity of NiO in the proposed Mars-van

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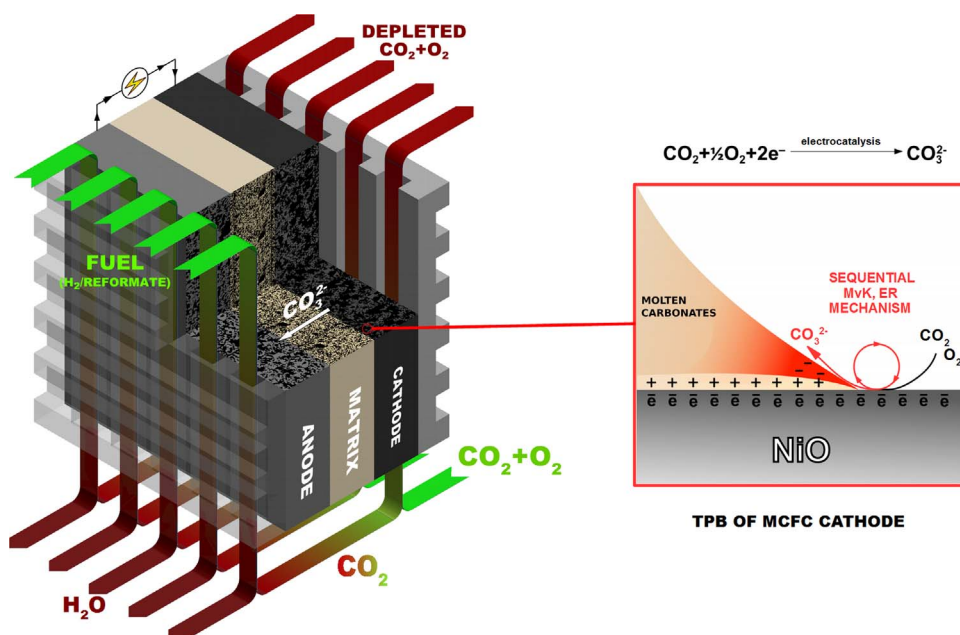


Fig. 1. Schematic of MCFC single cell which comprises of porous components: fuel electrode (anode), oxide electrode (cathode) and matrix separating electrodes and supporting molten (Li/K)₂CO₃ electrolyte. In *operando*, electrodes are fed with gaseous reactants (green flow lines), fully- or partially consumed or transformed into products (red flow lines), and promote electrode reactions resulting in energy generation process. In the atomic scale, the electrochemical catalytic reactions between CO₂ and O₂ may occur through sequential Mars-van Krevelen and Eley-Rideal mechanism on the surface of cathode in the vicinity of a triple phase boundary (TPB). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Krevelen (MvK) and Eley-Rideal (ER) sequential mechanism, based on adsorption and activation energies from our DFT calculations, we used the simplified microkinetic model together with Sabatier analysis. In this analysis, the coverages of free sites and adsorbed species are assumed to be optimal for each reaction step; therefore, the Sabatier rate will be considered as an exact upper limit of the reaction rate. Taking into account the potential energy diagram for $\text{CO}_2 + \frac{1}{2}\text{O}_2 + 2e^- \rightarrow \text{CO}_3^{2-}$ electrocatalytic reaction on O-terminated octopolar NiO(111), the reaction can be described by the following elementary steps:

R1: $\text{CO}_{2(\text{g})} + \cdot = > \text{CO}_{2(\text{ad})}$ (CO_2 chemisorption)

R2: $\text{CO}_{2(\text{ad})} + \text{O}\cdot = > \text{CO}_3^{2-}(\text{ad}) + \text{V}^\text{O}$ (Formation of CO_3^{2-} and oxygen vacancy)

R3: $\text{V}^\text{O} + \text{O}_{2(\text{g})} = > \text{O}_{2(\text{ad})}$ (O_2 chemisorption at oxygen vacancy site)

R4: $\text{O}_{2(\text{ad})} + \text{CO}_{2(\text{g})} = > \text{CO}_3^{2-}(\text{g}) + \cdot$ (CO_2 coupling with O_2 and CO_3^{2-} formation)

R5: $\text{O}_{2(\text{ad})} = > \text{O}_{(\text{ad})} + \cdot$ (O_2 dissociation)

R6: $\text{O}_{(\text{ad})} + \text{CO}_{2(\text{g})} = > \text{CO}_3^{2-}(\text{g}) + \cdot$ (CO_2 coupling with $\text{O}_{(\text{ad})}$ and CO_3^{2-} formation)

The adsorption energies and activation barriers for the foregoing reactions are listed in Table 1.

The electrophilic nature of molecular CO_2 and O_2 facilitates their adsorption onto the electron-rich cathode surface; therefore, we assume that the R1 and R5 steps are fast and can be considered as quasi-equilibrated. In the presence of molecular oxygen, the oxygen vacancy is instantly replenished (due to high adsorption energy) and hence, the

Table 1

The DFT computed parameters used in the microkinetic model. The data taken from Ref. [12].

Reaction	Adsorption energy [eV]	Activation barrier [eV]
R1	−0.76	0
R2	−	0.65
R3	−3.06	0
R4	−1.09	0
R5	−	0.39
R6	0.03	0

R3 step is very fast. Our calculations indicate that ER steps are barrierless and depend essentially on R3 (which is very fast), so the R4 and R6 can also be considered as quasi-equilibrated. Following the assumptions of Sabatier analysis, the rates of elementary reactions (R2 and R5) can be written:

$$r_2 = k_2 \theta_{\text{CO}_2} \theta_{\text{O}\cdot} \approx k_2 \theta_{\text{CO}_2}$$

$$r_5 = k_5 \theta_{\text{O}_2} \theta_{\text{O}}$$

where θ_{CO_2} , $\theta_{\text{O}\cdot}$, θ_{O_2} and θ_{O} denote the coverages of $\text{CO}_{2(\text{ad})}$, $\text{O}\cdot$, $\text{O}_{2(\text{ad})}$ and $\text{O}_{(\text{ad})}$, respectively.

The assumed optimal coverages that maximize r_2 and r_5 are $\theta_{\text{CO}_2} = 1$, $\theta_{\text{O}_2} = \theta_{\text{O}} = 0.5$, leading to our final expression of the Sabatier rate.

$$r_{\text{Sab.}} = \min\{k_2, 0.25k_5\}$$

The rate constant k for the elementary reaction can be obtained from the standard Arrhenius expression:

$$k = \nu \cdot \exp\left(\frac{-\Delta G_a}{k_B T}\right) = \nu \cdot \exp\left(\frac{-(\Delta E_a + \text{ZPE}_a - \Delta S_a T)}{k_B T}\right)$$

where ν is the pre-exponential factor, E_a is the activation barrier for the reaction, ZPE_a is zero-point energy change, ΔS_a is the entropy change, k_B is the Boltzmann constant and T is the temperature. The pre-exponential factor can be calculated using transition state theory from the entropy change between the initial and transition state of the reaction:

$$\nu = \frac{k_B T}{h} \cdot \exp\left(\frac{-\Delta S^*}{k_B T}\right)$$

The entropy of transition state is similar to the entropy of the initial state ($\Delta S^* = 0$), thus:

$$\nu = \frac{k_B T}{h}$$

Furthermore, we can assume that the change in zero-point energy is negligible compared to the activation barrier and the entropy of adsorbed species is significantly smaller than that in the gas phase ($\Delta S_a \approx S_g$). Having all necessary parameters from DFT and assuming: $T = 650^\circ\text{C}$ which is a typical for MCFC operation; $\text{CO}_2:\text{O}_2 = 2:1$ which is a typical feed gas ratio; $p = 1$ atm we can estimate the Sabatier rates and hence, catalytic activity of NiO under the most relevant

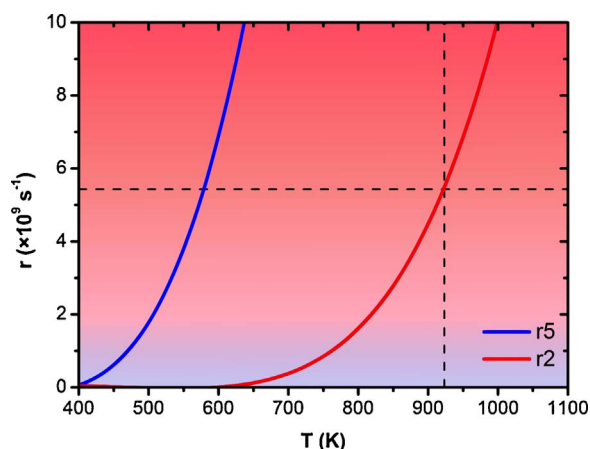


Fig. 2. Catalytic activity of O-terminated octopolar NiO(111) expressed as the Sabatier rates. The typical MCFC operation temperature and corresponding Sabatier rate is indicated by the dashed lines.

thermodynamic conditions of MCFC operation.

The calculated rate constants are: $k_2 = 5.43 \cdot 10^9 \text{ s}^{-1}$ and $k_5 = 2.68 \cdot 10^{11} \text{ s}^{-1}$. Finally, the Sabatier rate is: $r_{\text{Sab.}} = \min\{k_2, 0.25k_5\} = \{5.43 \cdot 10^9, 6.69 \cdot 10^{10}\} \text{ s}^{-1}$ (see Fig. 2). As can be seen, the Sabatier rates of $\sim 10^9 \text{ s}^{-1}$ indicate very fast kinetics of the electrochemical reactions occurring at the TPB of cathode. This in turn, proves that *in situ* oxidized nickel itself possesses high electrocatalytic activity when used as a cathode in MCFC; therefore, there is another factor responsible for overall performance of the MCFC cathode, supposedly associated with the melt chemistry. Our results provide an explanation why despite a great effort devoted to modify the chemical composition of cathode, substantial increase in the MCFC performance has not been observed, and the *in-situ* oxidized nickel remains state-of-the-art cathode material. At this stage one may ask, if the chemical tuning of cathode material does not allow to achieve higher performance of MCFC, is there any other possibility that can lead to the improved efficiency of cathodic process? We tentatively attribute molten carbonate and its complex chemistry as a space of exploration for the posed question. As commonly known, molten carbonate constitutes an electrolyte of MCFC and is responsible for transport of anionic species to the anode. A recently published article [13] for the first time involves the state-of-the-art first-principles molecular dynamics simulations, in order to clarify the nature of CO_2 transport in molten carbonate. According to the authors, the formation of pyrocarbonate anion ($\text{C}_2\text{O}_5^{2-}$) plays a crucial role in CO_2 transport that occurs through an oxo-Grothuss mechanism. Interestingly, there are a few reports in the literature showing that small addition of cations, e.g. Rb and Cs is leading to the increase in performance of MCFC [14,15]. On the basis of our results as well as the reported experimental and computational works, we can assume that apart from heterogeneous catalysis occurring at the TPB region of NiO cathode there is supposedly a homogeneous catalysis occurring in the melt, and the catalyst may be the solvated cations. Those specific cations probably enable faster formation of the unstable complexes, such as $\text{C}_2\text{O}_5^{2-}$ and as a result, increase the transport rate of anions to the anode of MCFC. Atomic-scale insight into the formation mechanism of the unstable complexes in the presence of different metallic cations may pave a way toward rational optimization of the melt chemical composition, and essentially to the better performance of MCFC.

3. Conclusions

In summary, we created a simplified microkinetic model and carried out Sabatier analysis to predict the catalytic activity of NiO in

heterogeneous electrocatalytic reactions of the cathode in MCFC. The recently proposed sequential Mars-van Krevelen (MvK) and Eley-Rideal (ER) mechanism occurring at the perimeter of TPB was taken under consideration. The *in situ* oxidized nickel is highly active towards electro-reduction of O_2 with simultaneous production of CO_2 under typical thermodynamic condition of MCFC operation. Our results provide a new insight into the complex chemistry of the cathode and explain why, despite a great effort devoted to modify its chemical composition, the *in-situ* oxidized nickel remains state-of-the-art cathode material. Based on profound analysis of our theoretical results and recent literature reports we postulate the existence of homogeneous catalysis in molten carbonate that may be responsible for better performance of MCFC cathode in the presence of foreign cations. This work provides an important indications toward the rational design of molten carbonate chemical composition and ultimately better efficiency of MCFC.

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